Absolute, On-Line Measurement of the Total Alkalinity of Seawater: A Tool for Evaluation of Global Climate Change Mediation Technologies for CO_2

An automated flux titration system was developed for the measurement of total alkalinity (TA) of seawater samples. This system yields absolute TA values without the need for periodic standardization of a standard acid solution. The determination is performed in an entirely closed system, which avoids uptake or loss of carbon dioxide (CO_2) from the sample during the sampling or titration steps. Systematic bias associated with equilibration with the surface atmosphere is thus eliminated.

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NIST is working o provide an absolute, shipboard-compatible measurement system of seawater TA for on-site monitoring. Together with separate pH measurements, the TA defines the capacity of seawater to accept CO_2, e.g., in sequestration of anthropogenic CO_2 to mediate global climate change (GCC).

Research has demonstrated the feasibility of the proposed approach. The principles of flux titration were tested and verified for synthetic seawater samples of known TA value in a closed system using absolute electrochemical (coulometric) generation of standard acid in a separate electrolyte stream. A novel iterative procedure was developed to obtain preliminary, "rough" values for the endpoint pH and approximate TA value. These preliminary values are required for the subsequent high-accuracy TA determination. The iterative procedure takes advantage of the fundamental differential equations, derived for this work, that describe the response time of the system. The unproductive period otherwise occupied in waiting for steady-state response is thereby utilized to provide rapid pre-characterization of the TA value. Fundamental hurdles to the operation of the system have been characterized. Approaches have been outlined to eliminate these hurdles and achieve reliable operation.

Impact: The system under development will yield a rugged, reliable measurement instrument for shipboard measurements of TA of seawater samples retrieved either by continuous or by grab sampling from depth, followed by subsequent sub-sampling at the surface. Results will be directly traceable to the Systèm international d'unités (SI), based on the fundamental chemical laws of electrolysis, stoichiometry, and acid-base titration theory. These results will enhance the understanding of global oceanic dynamics of the CO_2 system. This knowledge will aid worldwide efforts to predict the consequences of perturbations of the oceanic system that result from increases in atmospheric CO_2 levels or from intentional sequestration of CO_2 by deep water injection of anthropogenic CO_2.

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